NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

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THE SYNTHESIS OF METHYLENECYCLOBUTANE, SPIROPENTANE, AND 2-METHYL-1-BUTENE FROM PENTAERYTHRITYL TETRABROMIDE

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SUMMARY

Reduction of pentaerythrityl tetrabromide in ethanol with zinc in the presence of sodium carbonate and sodium iodide was found to yield methylenecyclobutane, spiropentane, and 2-methyl-1-butene. Yields were 46 percent methylenecyclobutane, 21 percent spiropentane, and 12 percent 2-methyl-1-butene. The reduction procedure described offers a method of preparing both methylenecyclobutane and spiropentane from the same reaction in yields comparable with individual methods of synthesis previously reported.

INTRODUCTION

Possible structures of the products from the reduction of pentaerythrityl tetrabromide in alcohol have been proposed in several conflicting reports since Gustavson first described the reaction in 1896 (reference 1). Gustavson assumed that the product of the reduction was vinyltrimethylene. Zelinsky (reference 2) and Rogowski (reference 3) concluded from their studies that the product was spiropentane. Philipow (reference 4) proposed that two compounds, methylenecyclobutane and methylcyclobutene, were formed in the reaction. Bauer and Beach reported (reference 5) that the results of an electron-diffraction study of the high-boiling product of the reduction indicated that the material could not possibly be spiropentane but was actually methylenecyclobutane. A large quantity of the reduction product was fractionated and by ozonolysis two constituents were shown to be present, the lower-boiling fractions consisting of 2-methyl-1-butene and the higher-boiling fractions methylenecyclobutane. (See footnote to reference 5.)

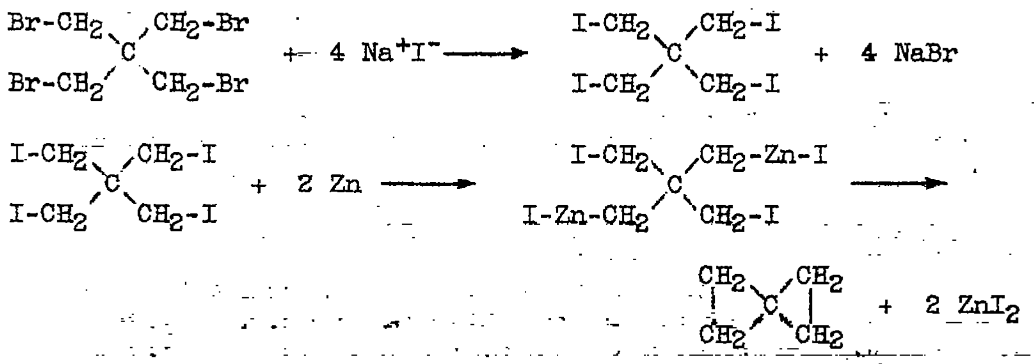
Murray and Stevenson (reference 6) reported in 1944 that the reduction of pentaerythrityl tetrabromide in molten acetamide yielded 2-methyl-1-butene, methylenecyclobutane, and a third component, believed to be spiropentane. Raman spectroscopic data lend credulence to their report of the isolation of spiropentane. Only a small quantity of the pure spiro compound was obtained.

Spiropentane might possibly prove to have unusual antiknock properties in the supercharged reciprocating internal-combustion engine because of its highly condensed structure. Consequently, a quantity of this hydrocarbon sufficient for engine tests was prepared at the Aircraft Engine Research Laboratory of the NACA during January to August 1945. More than 500 grams of spiropentane was isolated. Part of this material was used for engine testing; the rest was used for investigating the chemical and physical properties of this spiro hydrocarbon.

DISCUSSION OF THE REACTION

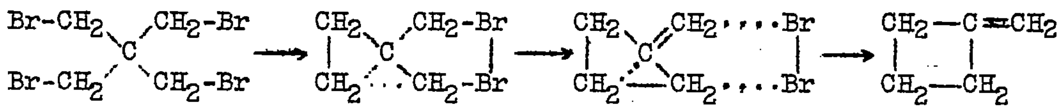
The reduction of pentaerythrityl tetrabromide in acetamide according to the procedure of reference 6 gave results comparable with those therein reported. Sublimation of the acetamide into the delivery tubes leading from the reaction flask to the chilled receivers proved troublesome in spite of attempts to heat the delivery tubes and to remove the acetamide by bubbling the effluent gases through water.

The ring closure of pentaerythrityl tetrabromide without the use of molten acetamide was believed to be feasible after a review was made of the reduction of 1,3-dichloropropane in alcohol with zinc in the presence of sodium carbonate and sodium iodide. The catalytic influence of iodide ions on the ring closure of 1,3-dichloropropane led to the belief that the reaction may occur through a Grignard-type synthesis (reference 7). The formation of spiropentane from pentaerythrityl tetrabromide might be considered to occur in the presence of iodide ions in an analogous manner:



Unlike the Grignard reaction the reduction of the halide appears to require a ready supply of iodide ions even after the reaction has once been started (reference 7). Sodium carbonate or acetamide conveniently reacts with zinc iodide to continuously regenerate the catalyst.

The formation of methylenecyclobutane from the reduction of pentaerythrityl tetrabromide occurs, according to Ingold (reference 8), through the following rearrangement:



PURIFICATION OF PRODUCTS AND DETERMINATION OF PHYSICAL CONSTANTS

The reduction products were fractionated in all cases through a 22-millimeter glass column, 7 feet in length, packed with $\frac{3}{32}$-inch single-turn glass helices. The column was rated at 100 theoretical plates at total reflux with methylcyclohexane – n-heptane test mixture.

Fractionation of the products from the reduction in molten acetamide and in ethanol yielded data showing the relation between index of refraction and percentage hydrocarbon recovered. Typical curves are shown in figures 1 and 2. Yields of the individual hydrocarbons were estimated from the fractional-distillation data.

The pure hydrocarbons were obtained in the following manner: Distillate from the first fractionation was combined into three cuts, (1) fractions having an index of refraction below n_D^{20} 1.4100; (2) fractions from n_D^{20} 1.4100 to n_D^{20} 1.4150; and (3) fractions above n_D^{20} 1.4150. Each of these three cuts was fractionated to obtain a sharper separation. Finally, material of constant index of refraction was combined and refractionated at a reflux ratio of 200:1 to obtain the pure hydrocarbons. In addition to the previously described procedure, spiropentane was treated with bromine as in reference 6 and fractionated over sodium metal.

Time-temperature freezing curves (figs. 3, 4, and 5) were obtained for the purest and the engine samples of methylenecyclobutane and spiropentane, and the purest sample of 2-methyl-1-butene, respectively, according to the procedure of reference 9. Boiling points were determined at 755 and 760 millimeters of mercury in a Cottrell apparatus as modified by Willard and Crabtree (reference 10). All temperature measurements were made with a NBS-calibrated platinum resistance thermometer. Indices of refraction were determined with a precision-type refractometer thermostatically controlled to $20^{\circ} \pm 0.1^{\circ}$ C. Densities were measured at 20° C by use of a 5-milliliter pycnometer.

SUMMARY OF EXPERIMENTAL RESULTS

A comparison of the products from the reduction of pentaerythrityl tetrabromide in acetamide and in ethanol is shown in table I. These data indicate that the reduction with zinc in ethanol in the presence of sodium carbonate and sodium iodide yields spiropentane in amounts comparable with those obtained by the molten-acetamide reduction method. The reduction in ethanol in the presence of sodium iodide and sodium carbonate also yields methylenecyclobutane in amounts comparable with those previously obtained by reducing the bromide in methanol (references 5 and 6).

Physical constants of the pure hydrocarbons and the material used for engine testing are compared in table II with physical constants of methylenecyclobutane, spiropentane, and 2-methyl-1-butene previously reported in references 6, 11, 12, and 13. The freezing point of the engine sample of methylenecyclobutane was found to be 0.06° C higher than the freezing point of apparently identical material later synthesized and purified. (See fig. 3.) The material later synthesized gave freezing points as high as -134.50° C, but these values were rejected because of the nonequilibrium nature of the time-temperature freezing curves. Freezing points as high as -106.96° C were obtained for spiropentane, but these values were also rejected because of the nonequilibrium nature of the freezing curves.

EXPERIMENTAL DETAILS

The methods described are typical of the procedures used. The pentaerythrityl tetrabromide was prepared in four runs, and the reduction was completed in nine runs of which those listed in table I are typical.

Pentaerythrityl tetrabromide. - The procedure described in reference 14 was followed.

A 12-liter three-necked flask was equipped with a 500-milliliter dropping funnel, a thermometer, and an air condenser leading to an aspirator-type gas trap. Twenty moles of crystalline pentaerythritol (2720 grams) was added into the flask and heated to 100° C in an oil bath. Forty moles (10,830 grams) of phosphorus tribromide was added to the pentaerythritol at such a rate that the temperature of the reaction mixture never exceeded 110° C. The addition of phosphorus tribromide required about 3 days.

After the addition of phosphorus tribromide was completed, the temperature of the reaction mixture was gradually raised over a period of 4 days to 175° C, during which time the color of the mixture changed from dark brown to brilliant orange. The reactants were kept at 175° C for 24 hours, then poured into a glass battery jar containing 12 liters of vigorously stirred ice water. The water was decanted and the solid product washed successively with four 4-liter portions of hot water and two 4-liter portions of ethanol. The impure orange pentaerythrityl tetrabromide was transferred to a large Büchner funnel and the alcohol removed. After air-drying on a metal tray for 24 hours, the crude product was exhaustively extracted with acetone in a 5-liter Soxhlet extractor to separate the product from the phosphorus impurities. The purified pentaerythrityl tetrabromide was recovered by chilling the acetone and filtering the white crystals on a Büchner funnel.

The yield of pentaerythrityl tetrabromide was 15.6 moles (6082 grams) or 78 percent of the theoretical amount.

Reduction of pentaerythrityl tetrabromide in ethanol. - The apparatus used in the reduction is shown in figure 6.

Into a 5-liter three-necked flask were introduced 2500 milliliters of absolute ethanol, 875 milliliters of water, 20 moles (1300 grams) of zinc dust, 5 moles (530 grams) of sodium carbonate, and 0.83 mole (125 grams) of sodium iodide. After the mixture was heated to refluxing temperature, 5 moles (1940 grams) of solid pentaerythrityl tetrabromide was added in small portions from a solid-addition flask. Each addition of the tetrabromide caused frothing of the reaction mixture and flooding in the reflux condenser. As the frothing subsided, more tetrabromide was added, the total addition time being about 4 hours. The reaction mixture was vigorously stirred during the entire reaction period to prohibit the zinc dust from caking on the walls and bottom of the reaction flask.

After the reaction mixture was heated for 1 hour to remove the last traces of hydrocarbon, the product was poured from the chilled receivers into 2 liters of cold water contained in a 6-liter separatory funnel to remove any alcohol that had distilled over with the hydrocarbons. A significant amount of vaporization of low-boiling material accompanied the washing operation. The remaining product was dried over calcium sulfate and fractionated.

The yield of hydrocarbon products was 4.48 moles (305 grams) or 90 percent of the theoretical amount. The composition of the product, estimated from fractional-distillation data, was 53 percent methylenecyclobutane, 22 percent spiropentane, and 13 percent 2-methyl-1-butene. A small amount of unidentified material boiling from 19.5° to 27° C was also obtained.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, December 29, 1945.

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TABLE I - COMPARISON OF PRODUCTS FROM THE REDUCTION OF PENTAERYTHRITYL TETRABROMIDE IN ACETAMIDE AND IN ETHANOL

Reduction solvent	Moles of reactants				Total yield of hydrocarbons		Yield of individual hydrocarbons in the mixture					
	Penta-erythritol tetra-bromide	Zinc dust	Sodium car-bonate	Sodium iodide	(grams)	(per-cent)	Methylene-cyclobutane		Spiropentane		2-Methyl-1-butene	
							(grams)	(per-cent)	(grams)	(per-cent)	(grams)	(per-cent)
Acetamide	2	7	2.5	0.25	60	44	18	13	23	17	8	6
	1	6	1.2	.16	35	51	3	4	15	22	7.5	11
Ethanol	5	20	5.0	0.83	305	90	180	53	76	22	43	13
	10	48	18.0	3.6	600	88	305	45	136	20	74	11
	5	20	5.0	.83	275	81	146	43	70	21	40	12
	5	20	5.0	.83	290	85	149	44	76	22	40	12

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TABLE II - PHYSICAL CONSTANTS OF METHYLENECYCLOBUTANE, SPIROPENTANE, AND 2-METHYL-1-BUTENE

Compound	Source of constants	Freezing point (°C)	Boiling point (°C)		Index of refraction n_D^{20}	Density at 20° C (grams/ml)
			755 mm	760 mm		
Methylene-cyclobutane	Reference 11	---------	[a]41.39	-------	1.4210	0.7401
	NACA pure sample	-134.68	42.02	42.22	1.42087	.7401
	NACA engine sample	-134.62	----------	42.25	[b]1.4208	.7399
Spiropentane	Reference 6	---------	[a]36.3-38.5	------	1.4117	0.755
	NACA pure sample	-107.05	38.84	39.03	1.41220	.7551
	NACA engine sample	-107.28	38.81	39.01	[b]1.4121	.7552
2-Methyl-1-butene	Reference 12	---------	[c]31.05	-------	1.3777	0.6504
	Reference 13	-137.560	----------	31.10	1.3778	.6504
	NACA pure sample	-137.50	30.93	31.12	1.37781	.6504

[a]750 mm pressure.
[b]With Abbé refractometer; other NACA values taken with precision-type refractometer.
[c]Pressure not given.

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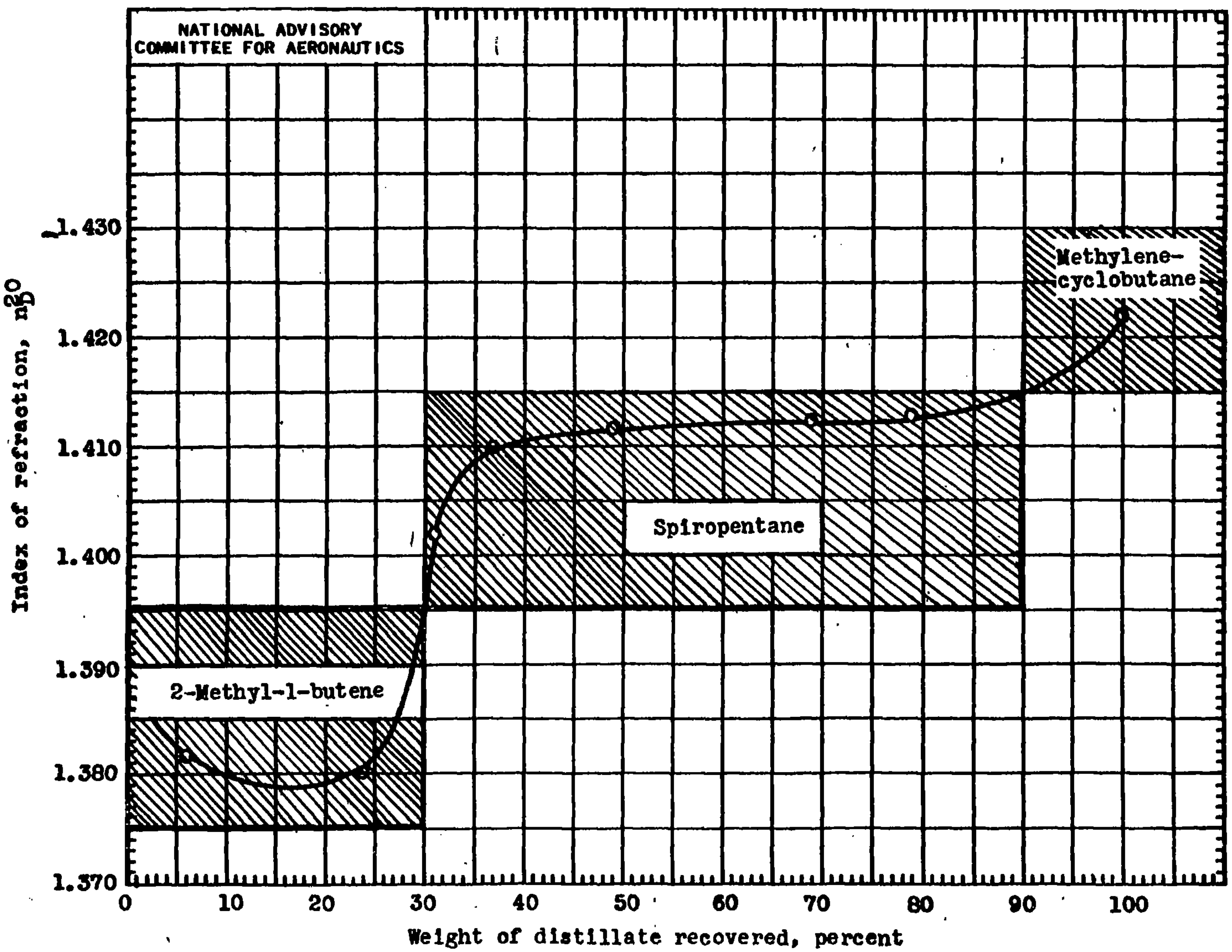


Figure 1. - Composition of product from the reduction of pentaerythrityl tetrabromide in molten acetamide in the presence of sodium carbonate and sodium iodide.

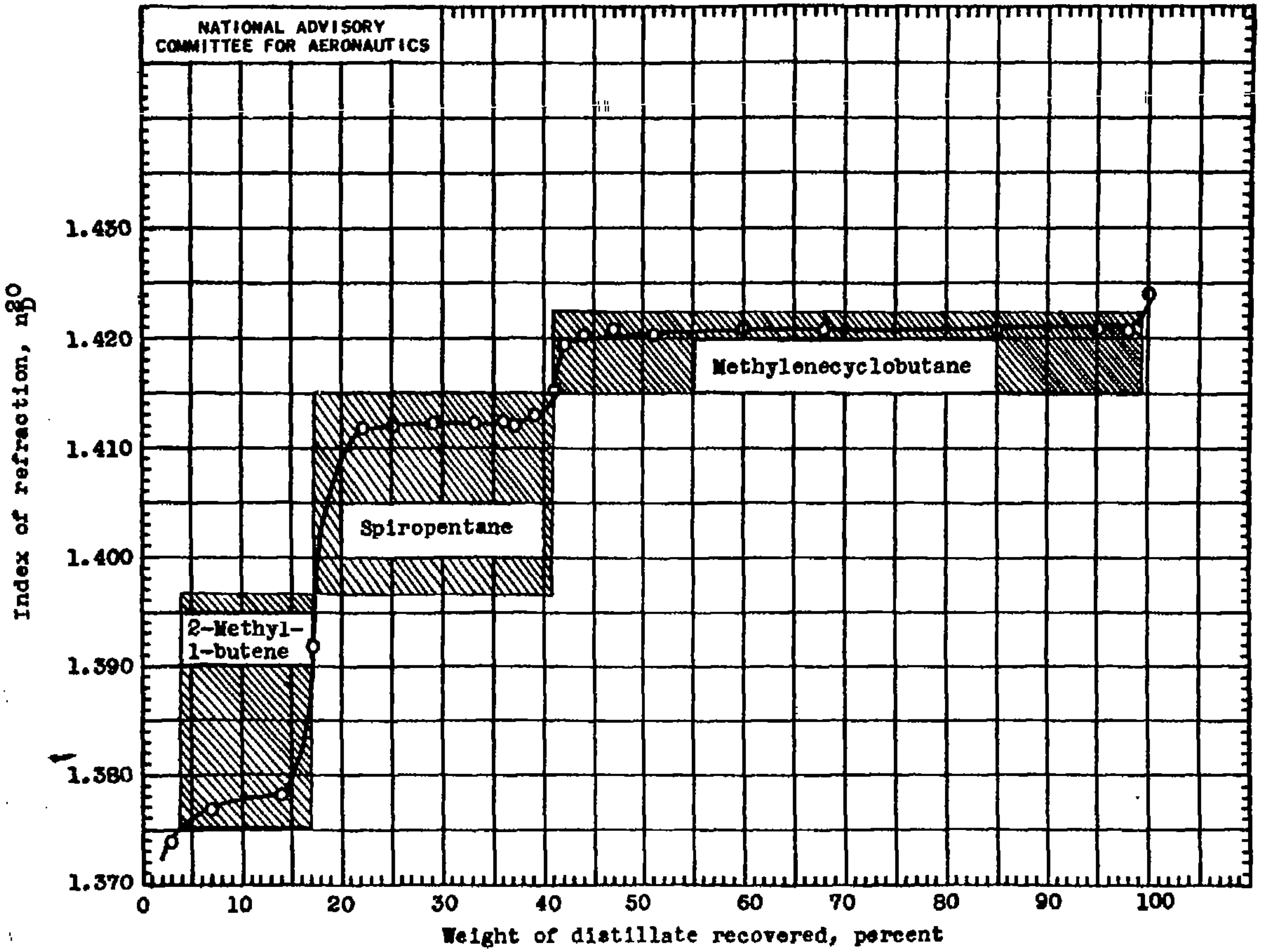


Figure 2. - Composition of product from the reduction of pentaerythrityl tetrabromide in ethanol in the presence of sodium carbonate and sodium iodide.

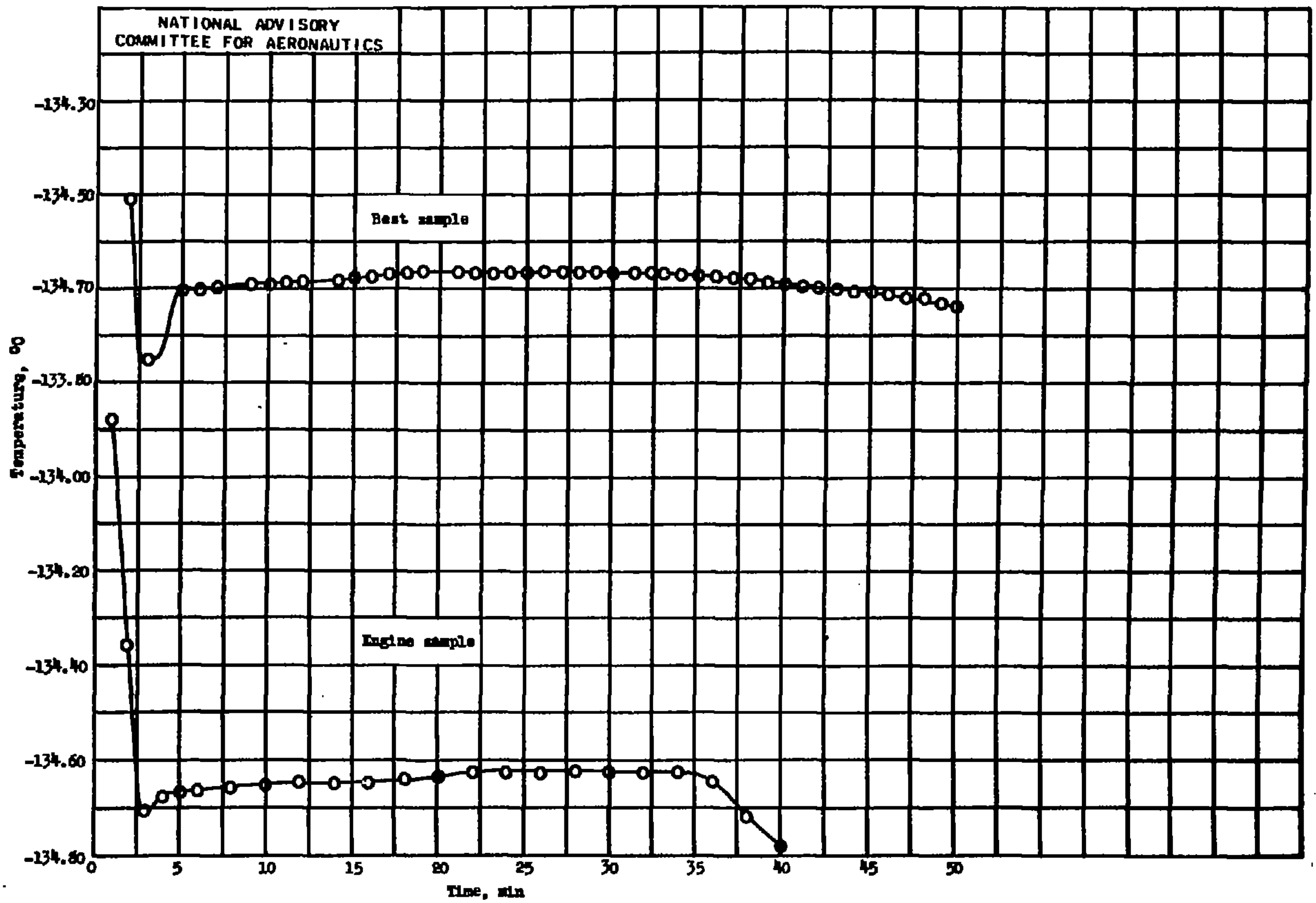


Figure 3.- Time-temperature freezing curve of methylenecyclobutane.

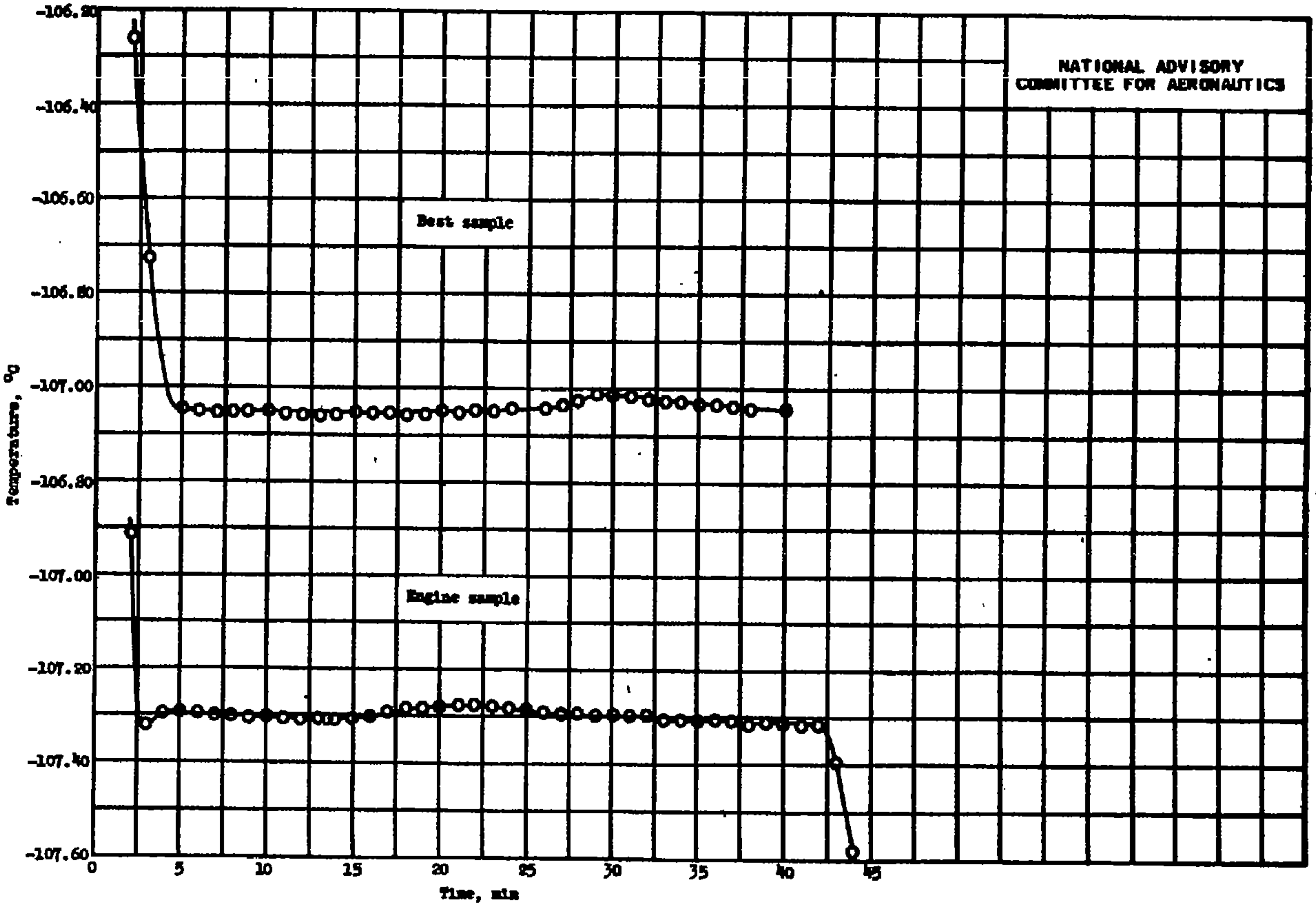


Figure 4.- Time-temperature freezing curve of spiropentane.

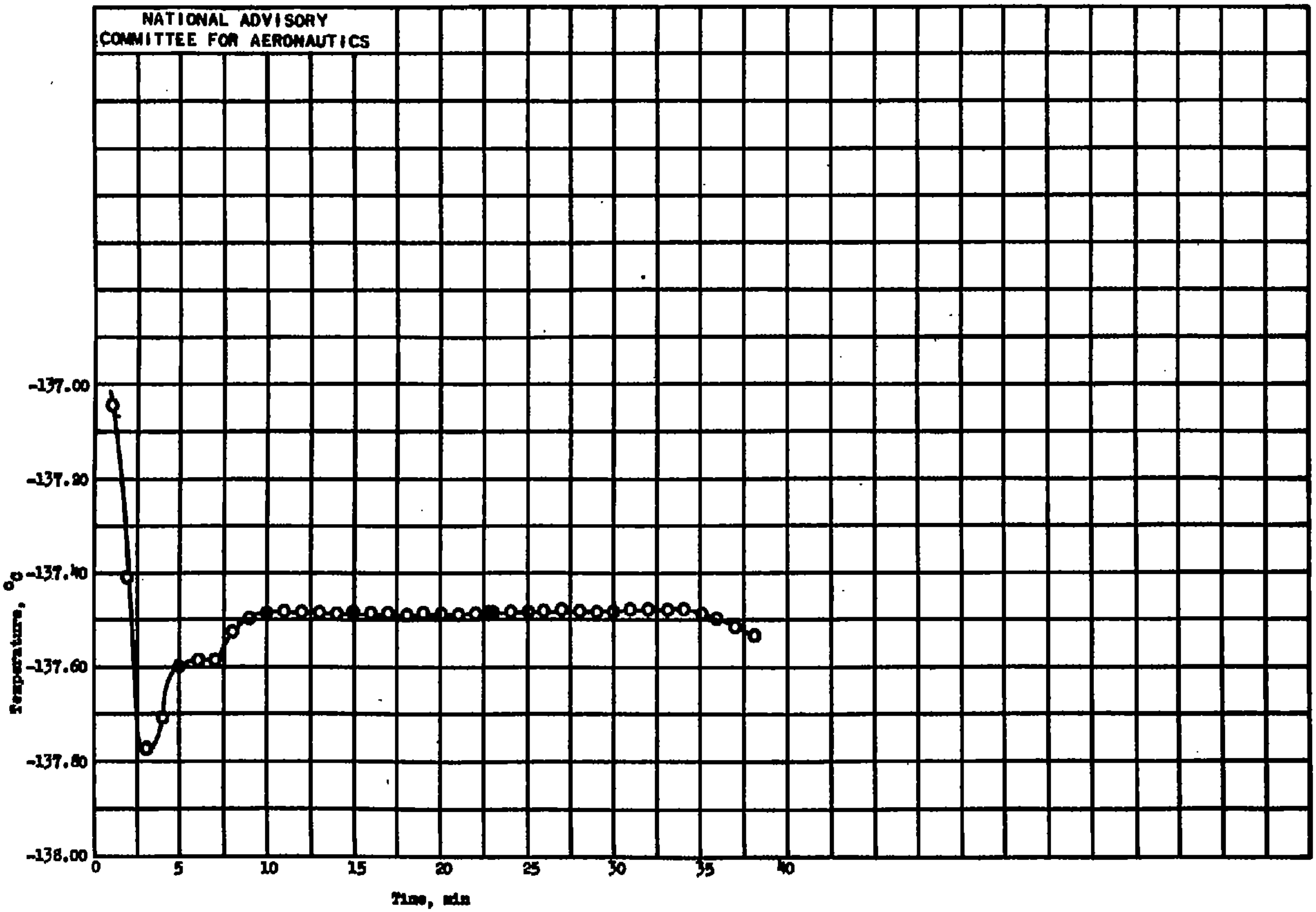
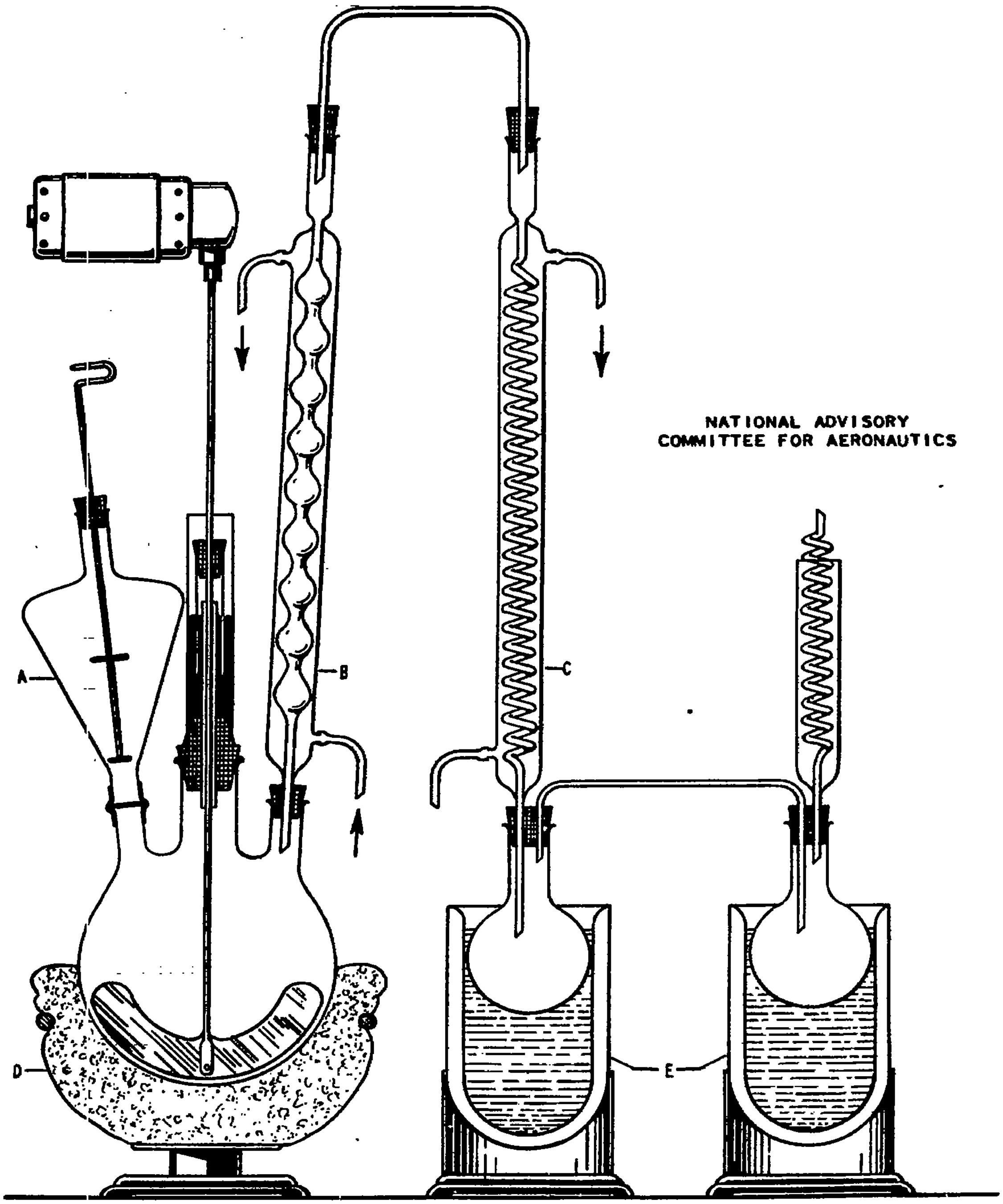


Figure 5.- Time-temperature freezing curve of 2-methyl-1-butene.



A Addition flask for introducing solid pentaerythrityl tetrabromide.
B Condenser. Temperature of cooling water: 50° C.
C Condenser. Temperature of cooling water: 10° C.
D Heating mantle.
E Dewar flasks containing solid CO_2 - acetone cooling mixture.

Figure 6. - Apparatus for reduction of pentaerythrityl tetrabromide in ethanol.